AP

09/743479
PCT/AU99/00564

AUSTRALIA

5

Patent Office
Canberra

REC'D 09 AUG 1999
WIPO PCT

I, KIM MARSHALL, MANAGER EXAMINATION SUPPORT AND SALES, hereby certify that the annexed is a true copy of the Provisional specification in connection with Application No. PP 4637 for a patent by FOOD & PACKAGING CENTRE MANAGEMENT LIMITED filed on 14 July 1998.

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

COMMONWEALTH OF AUSTRALIA
AUSTRALIA
PATENT OFFICE

WITNESS my hand this Second day of August 1999

KIM MARSHALL
MANAGER EXAMINATION SUPPORT AND SALES

AUSTRALIA
Patents Act 1990

PROVISIONAL SPECIFICATION

PP filed July 1998

Invention Title : **Biocidal packaging system**

Applicant: **Food & Packaging Centre Management Limited**
[A C N 070 675 464]

Inventors: Penny Corrigan
Victor Christov

The invention is described in the following statement:

Biocidal Packaging System

This invention relates to improvements in retarding unwanted biological growth in food packaging particularly in retarding fungal or mould growth in packaged fruit especially table grapes.

Background to the invention

Where table grapes are stored for prolonged periods or where they are transported over long distances, the continued or repeated application of a fungicide to slow the growth of Botrytis mould is required.

Australian patent 565243 disclosed incorporating a fungicide in a packaging film of polyethylene and heating the film to release the fungicide. Australian patent 646013 discloses a wrapping film for use in retarding fungal decay of citrus fruits which incorporates a fungicide in a first resin layer of a high melt temperature [170-240°C] and then blending it with a second resin of lower melt temperature. This ensures that the fungicide is released slowly.

In Australia the current method of control is to package table grapes in a waxed corrugated cardboard box having an inner plastic liner bag. A sulphur dioxide releasing pad or sachet is placed inside the package. Such a system is disclosed in USA patent 3559562. Although this has given satisfactory results there are a number of disadvantages. The rate of release of sulfur dioxide is not well controlled especially if there are temperature fluctuations during storage. High levels of Sulfur dioxide cause bleaching of the grapes with the consequence that their sale price is lowered. Further, high residue levels of sulfite in the grapes can cause health problems for a proportion of the population. Another difficulty with the present method is the localized release of sulfur dioxide within the package resulting in considerable variation of sulfur dioxide concentration.

It is an object of this invention to provide a means of releasing sulfur dioxide at a constant or zero order rate so that a minimally effective dosage rate can be achieved to reduce the disadvantages of using sulfur dioxide.

Brief description of the invention

To this end the present invention provides a block, pad or film of a polymer blend which contains at least one polymer having a substantially different water transmission rate to at least one other polymer in the blend and there being dispersed through the polymer blend an antifungal agent activated by the presence of moisture.

This invention is predicated on the discovery that the release rate of water activated fungicides such as sodium metabisulfite can be controlled by controlling the proportions of polymers having high and low water transmission rates. This invention is predicated on the realisation that there are two polymer properties which affect the release rate of sulfur dioxide, the rate at which water or water vapour penetrates the polymer to contact the bisulfite and the rate of transmission of the sulfur dioxide through the polymer. This discovery means that slow release preparations can now be provided that have a lower release of sulfur dioxide without being below the concentration which inhibits fungal growth. The release rate can also be adjusted to suit the rate required by different fruit varieties.

Where the water activated fungicide is sodium metabisulfite the polymer blend preferably is processable at temperatures below 150°C which is the decomposition temperature of the sodium metabisulfite. Potassium metabisulfite as the fungicide allows processing temperatures below 190 °C to be used but it has a slower release rate and a lower overall conversion per mole.

The polymer blend is preferably an olefine polymer with a polymer containing hydrophillic groups. The ratio of hydrophobic to hydrophillic polymer can be determined by simple trials. Preferably the polymer blend includes an ethylene/vinyl alcohol copolymer [EVA] as the polymer with high release rate and a linear low density polyethylene[LLDPE] as the polymer with a low water release rate. A blend of these two polymers EVA / LLDPE within the range of 30:70 to 80:20 is usually effective. A preferred blend contains equal amounts of EVA and LLDPE.

The fungicide can be any active fungicide that allows the active agent to migrate through the polymer in a sustained manner. Water activated fungicides are preferred for the polymer blend of this invention. Sulfur dioxide generating agents are preferred and in particular bisulfite compounds the most preferred being

sodium metabisulfite. The metabisulfite is in finely divided form, but there is no criticality to the particle size of the compound. The amount of the metabisulfite in the polymer blend must be sufficient to maintain a sustained release of sulfur dioxide over a period of up to 8 weeks. Usually a content of 10% to 30% by weight has been found to be adequate.

In another aspect of this invention there is provided a package for transporting and storing fruit preferably table grapes which includes

1. a container ;
2. optionally a water absorbent material lining said container;
3. optionally, a plastic liner between the container walls and said absorbent material;
4. disposed adjacent the fruit a film pad or block of a polymer blend containing a moisture activated antifungal agent wherein the polymer includes at least one polymer having a water transmission rate substantially different to that of at least one other polymer of said blend.

It has been found that the presence of a water absorbent material such as corrugated paper wadding appears to stabilize the release rate of sulfur dioxide presumably by reducing the humidity levels in the container. Some wadding materials may also act as a sink for sulfur dioxide.

Detailed description of the invention

A preferred embodiment of the invention will now be described.

Polymer blends of 30% Low density polyethylene [LDPE] with 70 % of a copolymer of ethylene and vinyl alcohol[EVA] {liner 1}and 50% LDPE with 50% EVA,[liner 2] each containing 15% sodium metabisulfite, were formed into film and converted to liner bags for grape boxes.

These were then tested as box liners in a field trial using Thompson seedless grapes. Grapes picked the previous day and stored in the cool room were packed in boxes with conventional high density polyethylene liners [HDPE] and the liners of this invention. All boxes were returned open to the coolroom and left till the grapes reached <2°C. Bags were then closed and the lids added with addition of SO_2 pads to the conventionally lined boxes and corrugated wadding as required.

The 54 boxes were loaded onto a pallet and trucked overnight. On arrival they were split into sub-trials and subjected to two different storage regimes

1. a temperature profile simulating air freight from Melbourne to an Asian destination
2. a temperature profile simulating sea freight from Melbourne to an Asian destination

Air freight simulation

The treatments in this subtrial were

AA PE liner with SO_2 pad [Oskuvid] plus corrugated wadding

AB PE liner with corrugated wadding

AC liner 1 with corrugated wadding

AD liner 2 with corrugated wadding

Each treatment had six replicates [24 boxes in all]

On arriving from the overnight trucking the boxes were placed in a holding bay and left at ambient temperatures for two days. The temperature in the boxes reached about 17 °C. the boxes were then placed in a coolroom at 2-3 °C for 10days. SO_2 levels in half the boxes were measured several times during storage including when at the high temperature [see figure 1].The higher temperatures increased the SO_2 release rates from liners 1 and 2 and more so from 1 [AC] than 2 [AD]. The release rates dropped rapidly with temperature when returned to the cool room. In contrast the SO_2 pad AA showed a marked increase in SO_2 levels after return to the cool room due to condensation inside the pads [see figure 1].

At the end of the storage period the grapes were removed, weighed and three bunches from each box taken for assessment for rot and stem condition. These bunches were from the top centre, top corner and bottom corner positions in the box. After a further three days storage at 21 °C these bunches were again assessed for rot bleach and stem condition.

Ex-store assessment

Table 1 Quality assessment parameters on removal from cold storage

treatment	% rot	Stem condition	Average weight of grapes [kg]
AA	0	1.4	10,12
AB	0	2.6	10.11
AC	0	1.6	10.06
AD	0	1,7	9.88

The weights measured indicate that liner 2 may not be a sufficient water barrier although the stem condition is not significantly different from the other treatments.

Ex-marketing assessment

Table 2 Quality assessment after 3days at 20 °C

Treatment	% bleach [berries]	% rot	Stem condition	SO_2 exposur [ppm.days]
AA	5.9	0	2.1	218
AB	0	2.8	4.3	0
AC	9.3	0.1	3.8	136
AD	10,0	0.1	4.4	23
LSD [p<0.05]	5.0		0.8	

Bleach in the bunches taken from different positions in the box were also analysed.

Table 3 Bleach levels at different box positions

Position	AA	AC	AD
Top centre	8.8	9.9	9.4
Top corner	4.8	8.5	9.8
Bottom corner	4.0	9.5	10.8

LSD [p<0.05] = 6.1

All the SO_2 treatments were successful in preventing the growth of rots, however despite the measured differences in SO_2 levels delivered in the different treatments, there was no statistical difference in the total amount of of bleach observed. Liners 1and 2 both delivered SO_2 in a more even manner throughout the

box as no positional differences were observed. In contrast the oskuvid pad [AA] caused greater bleaching in the top centre than in the bottom bunch. Previous trials have shown that pads show a distinct gradient with high levels at the top near the pad and low levels at the bottom of the box.

Sea Freight Temperature simulation

Treatments in this sub trial were

SA PE liner with SO_2 pad [Oskuvid] plus corrugated wadding

SB PE liner with corrugated wadding

SC liner1 with corrugated wadding

SD liner 2 with corrugated wadding

SE liner 1 with no added wadding

On arriving in Melbourne after the overnight trucking these boxes were placed in a coolroom at 5 °C for two days, then moved to a coolroom at 2-3 °C for 4 weeks. SO_2 levels in half the boxes were measured several times during storage. These are shown in figure 2.

From the graph comparing SC with SE it is clear that the wadding has a large effect on SO_2 levels in the packaging. This may be due to absorption of sulfur dioxide by the wadding and/or to the wadding modifying humidity levels.

At the end of the storage period grapes were removed and four bunches were taken from four different positions in each box for assessment of rot and stem condition. After a further 3 days storage at 21 °C, these bunches were again assessed for rot, bleach and stem condition. A more detailed bleach assessment was also undertaken to assess severity of bleach as well as the % of bleached grapes [by weight]. For each bunch the bleached grapes were separated into three groups representing severity of bleach:

1. < 10% of grape surface area
2. < 25% and > 10% of grape surface area
3. > 25%% of grape surface area

These were then weighed and calculated as a % of the bleached grapes.

Ex-store assessment

Table4 Quality assessment parameters on removal from cold storage

treatment	% rot	Stem condition	Average weight of grapes [kg]
SA	0	1.25	10.05
SB	1.84	3	10.39
SC	0	1.33	10.00
SD	0.16	1.54	9.92
SE	0	1.71	9.97

Again liner 2 is showing greater water loss than the conventional treatments. All the treatments with c successfully controlled the growth of Botrytis.

Ex-Marketing assessment

Table 5 Quality assessment after 3days at 20 °C

Treatment	%bleach [berries]	Bleach [severity]	% rot	Stem condition	SO_2 exposure [ppm.days]
SA	22.7	0.398	0	2.3	351
SB	0	0	12.7	4.7	0
SC	16.5	0,188	0.2	3.5	67
SD	8.4	0.093	0.2	3.6	25
SE	39.6	0.539	0	3.5	236
LSD [p<0.05]	6.3	0.82		0.76	

The positional effects are shown in table 6

Table 6 Bleach severity according to bunch position in box

	SA	SC	SD	SE
Top centre	0.54	0.20	0.07	0.46
Top corner	0.41	0.14	0.10	0.57
Middle	0.33	0.15	0.05	0.52
Bottom corner	0.31	0.26	0.16	0.61

LSD[p<.05] = 0.16 [for comparing across treatments]

= 0.17 [for comparing within treatments]

The bottom bunches of liner 1 without wadding were the most severely bleached. Liner 2 was the most effective at controlling rot whilst minimising bleaching. It is surprising that bleaching was observed at such low SO_2 levels. Temperature may have a significant effect on susceptibility to bleaching since these grapes were not stored at the preferred 0 °C.

From the above it can be seen that the present invention can minimise bleach damage without compromising the retardation of rot.

CLAIMS

1. A package for transporting and storing fruit preferably table grapes which includes

a) a container ;

b) optionally a water absorbent material lining said container;

c) optionally, a plastic liner between the container walls and said absorbent material;

d) disposed adjacent the fruit, a film pad or block of a polymer blend containing a moisture activated antifungal agent wherein the polymer includes at least one polymer having a water transmission rate substantially different to that of at least one other polymer of said blend.

2) A block, pad or film of a polymer blend which contains at least one polymer having a substantially different water transmission rate to at least one other polymer in the blend and there being dispersed through the polymer blend an antifungal agent activated by the presence of moisture.

3) A liner film for use in packaging table grapes said film including a major portion of an ethylene /vinyl alcohol copolymer, a minor portion of a low density polyethylene and an effective amount of an antifungal agent preferably from 10 to 30% of sodium metabisulfite.

ABSTRACT

A liner for a table grape box consists of a polymer blend of low density polyethylene and a copolymer of ethylene and vinyl alcohol. The film incorporate sodium metabisulfite. In response to the moisture present in the box sulfur dioxide is released at a constant rate without the usual bleaching and health problems associated with excess generation of sulfur dioxide.

Figure 1. Average SO_2 Levels in Treatments

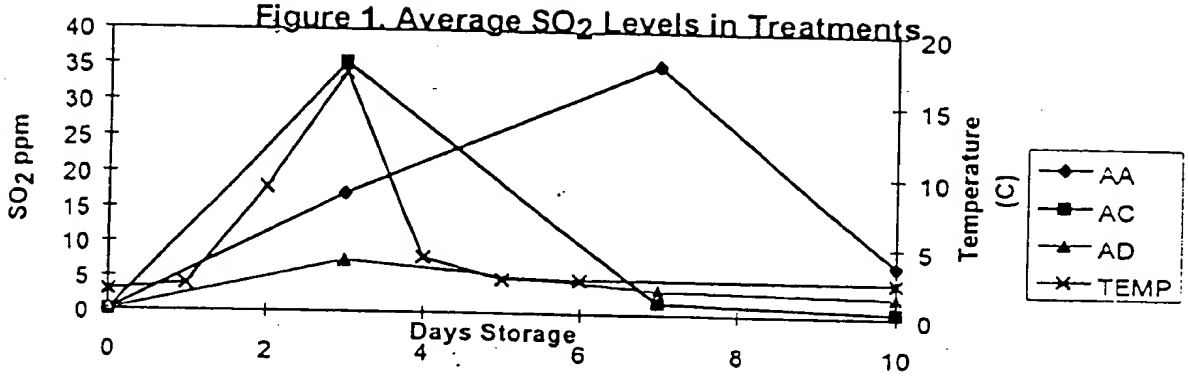

Figure 2. Average SO_2 Levels in Seafreight Trial